DEMULSIFICATION OF WATER-IN-CRUDE OIL EMULSIONS VIA MICROWAVE HEATING TECHNOLOGY

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ABSTRACT

The traditional ways of breaking emulsions using heat and chemicals are disadvantageous from both economic and environmental perspectives. In this study, an alternative and cost effective technology for high frequency energy separation of oil emulsions has developed. The potentials of microwave technology in demulsification of water-in-crude oil emulsions are investigated. After exposing the emulsion to the microwave electromagnetic (EM) field, molecular rotation, and ionic conduction due to the penetration of EM into the emulsion are responsible for the internal heating. In this study, microwave demulsification was applied in a 50-50 %, 30-70 % and 10-90 % water-in-oil emulsions with microwave exposure time varied from 20-200 sec. The temperature rise at a given location was almost horizontal (linear). The average rates of temperature increase of 50-50 %, 30-70 % and 10-90 % water-in-oil emulsion are 1.042, 0.582 and 0.218 ^{o}C/sec, respectively. The rate of temperature increase of emulsions decreased at higher temperature due to decreasing dielectric loss of water. Viscosity increases with amount of surfactant used, whereas, viscosity and shear stress decreases as temperature and rpm increased.

ABSTRAK

Kaedah-kaedah tradisional yang biasa digunakan dalam pemisahan air daripada emulsi air dalam minyah mentah seperti pemanasan dan penggunaan bahan kimia memdatangkan masalah dari segi ekonomi dan alam sekitar. Dalam kajian ini, cara alternatif dan teknologi yang murah untuk pemisahan emulsi dari segi tenaga berfrekuensi tinggi dikaji. Keupayaan teknologi gelombang mikro dalam pemisahan emulsi air dalam minyak tanah. Setelah mendedahkan emulsi kepada medan electromagnet gelombang mikro, putaran molekul dan ion konduksi berlaku kerana penetrasi gelombang mikro ke dalam emulsi bertanggungjawab atas pemanasan dalaman. Dalam kajian ini, pemisahan emulsi dengan penggunaan gelombang mikro digunakan ke atas emulsi pada kadar 50-50%, 30-70% dan 10-90% dengan pendedahan gelombang mikro pada variasi masa dari 20 hingga 200 saat. Peningkatan suhu pada lokasi berlainan dalam emulsi adalah lebih kurang sama (linear). Peringkat rata-rata kenaikan suhu untuk emulsi pada kadar 50-50%, 30-70% dan 10-90% adalah 0.886, 0.526 dan 0.395 ^{o}C/sec masing-masing untuk radiasi 540W, manakala 1.042, 0.582 dan 0.218 ^{o}C/sec untuk radiasi720W. Pada suhu tinggi, kadar peningkatan suhu emulsi berkurang kerana kehilangan dielektrik air berkurang. Kelikatan emulsi meningkat dengan jumlah surfaktan yang digunakan, manakala, kelikatan dan tegangan ricih emulsi menurun apabila suhu dan rpm bertambah.

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LIST OF ABBREVIATION

mw	:	microwave
o/w	:	oil-in-water emulsion
w/o	:	water-in-oil emulsion
rpm	:	rotations per minute
SDDS	:	Sodium Dodecyl Sulfate
LSWR	:	Low Sulfur Wax Residue
MESB	:	Mechanical Emulsion Breaker
R/A	:	Resin to Asphaltene ratio
EM	:	Electromagnetic
SARA	:	Saturated Asphaltene, Resin and Aromatic

LIST OF SYMBOLS

V_w	:	Settling velocity (cm/sec)
ρ_w	:	Density of dispersed phase (g/cm^3)
ρ_o	:	Density of continuous phase (g/cm^3)
g	:	Gravity
D	:	Droplet diameter (cm)
Po	:	Microwave surface power (W)
A	:	Sample container area (cm^2)
m	:	Mass of sample (g)
P_z	:	Microwave power transmitted (W)
α_E	:	Electromagnetic attenuation factor (cm^{-1})
f	:	Frequency of incident microwaves
δ	:	Loss tangent
q_{MW}	:	Volume rate of heat generation (W/cm^3)
λ_m	:	Wavelength (cm)
D_m	:	Penetration depth (cm)
ε''r	:	Dielectric loss
ε'r	:	Dielectric constant
c	:	Speed of light (cm/sec)
h	:	Convective heat transfer coefficient (cal/s cm^2 ^{o}C)
v	:	Volume of water separated (cm^3)
T_m	:	Temperature of emulsion ^{o}C
T_a	:	Temperature of ambient ^{o}C

σ	:	Stefan-Boltzmann constant
φ	:	Volume fraction of emulsified water
ε	:	Emissivity of surface
Cp_m	:	Heat capacity of emulsion (cal/g^{o}C)
ρ_m	:	Density of emulsion (g/cm^3)

CHAPTER 1

INTRODUCTION

1.1 Background of the Study

The complex nature of the emulsions of water in crude oil is one of the main drawbacks to the development of techniques suitable for demulsification and phase separation in the oil industry. In spite of the huge recent efforts for developing dependable and efficient demulsification techniques, most emulsions of water in crude oil cannot be broken in reduced times. Actually the demulsification operation is a key process for removing water from crude oil in refineries (Coutinho *et al.,* 2007). Specifically, in order to remove water from crude oil up to acceptable levels, there is a need of demulsification (dehydration) stages in the desalting plants generally encountered in environmental technology, painting, coating and petroleum refineries.

One of the most widely used methods in treating water-in-oil emulsions is chemical destabilization, which involves the use of chemical additives to accelerate the emulsion breaking process. For economic and operational reasons, it is necessary to separate the water completely from the crude oil before transporting or refining. There are many methods for the demulsification process, such as gravity separation, electrostatic coalescence, centrifugal and filtration methods.

In this Research Project, the microwave heating technology as an alternative demulsification process will be used. Electromagnetic radiation in the frequency range 300MHz to 300 GHz are known as microwaves, microwave energy is non-iodizing radiations that cause molecular motion by migration of ions and dipole rotations, but does not cause changes in molecular structure and wavelengths ranging from a few centimeters to a few millimeters (Abdurahman *et al.*, 2007). Microwave heating offers a faster processing rate because of its volumetric heating effects. In conventional thermal processing, energy is transferred to the material through convection; conduction and radiation of heat the surfaces of the material. In contrast, microwave energy is delivered directly to materials through molecular interaction with the electromagnetic field. In heat transfer, energy is transferred due to thermal gradients, but microwave heating is the transfer of electromagnetic energy to thermal energy and is energy conversion, rather than heat transfer. This difference in the way energy is delivered can result in many potential advantages to using microwaves for processing of materials. The transfer of energy does not rely on diffusion of heat from the surfaces and it is possible to achieve rapid and uniform heating of thick materials (Abdurahman *et al.*, 2007).

Below follows a list of abbreviations and concepts that needs to be defined and clarified. These concepts will be used throughout the paper and therefore it is important to explain how they will be used to prevent misinterpretations as well as increase the understanding of the paper.

a) **Separation** is done to separate two or more things which are in a mixture form.

b) **Crude oil** is defined as a type of oil in a nature state that has not yet been treated. Geologists generally agree that crude oil was formed over millions of years from the remains of tiny aquatic plants and animals that lived in ancient seas. There may be bits of brontosaurus thrown in for good measure, but the petroleum owes its existence largely to one-celled marine organisms. It is the particular crude oil's geological history that is most important in determining its characteristics, which is why crude oils formed in similar marine deposits at different continents can resemble each other. Regions characterized by different marine deposits, pressures and temperatures may however produce crude oil with a great variety in appearance, from honey-colored, greenish to black, light or heavy, waxy or not (A. Hannisda, 2005).

c) **Emulsion** is a mixture of two immiscible (unblendable) liquids. One liquid (the dispersed phase) is dispersed in the other (the continuous phase). Many emulsions are oil/water emulsions, with dietary fats being one common type of oil encountered in everyday life. Emulsions tend to have a cloudy appearance, because the many phase interfaces (the boundary between the phases is called the interface) scatter light that passes through the emulsion. Emulsions are unstable and thus do not form spontaneously. Over time, emulsions tend to revert to the stable state of the phases comprising the emulsion. Surface active substances (surfactants) can increase the kinetic stability of emulsions greatly so that, once formed, the emulsion does not change significantly over years of storage.

d) **Microwave** is a very short electromagnetic wave used for sending information by radio or radar.

1.2 Problem Statement

Water is normally present in crude oil reservoirs or is injected as steam to stimulate oil production. Water and oil can mix while rising through the well and when passing through valves and pumps to form in most cases relatively stable dispersions of water droplets in crude oil, which are usually referred to as oil field emulsions (Abdurahman *et al.*, 2007). 90% to 95% of the world crude oil is produced in the form of emulsion. The presence of water in oil creates a lot of problems, due to economic reasons and pipeline corrosion; it is required to separate water completely from the oil before sending oil for processing. The conventional methods for this process are usage of chemicals and high heat to separate water from oil and then send the oil to the refinery and water to the treatment plant processes, but these methods are expensive. So, microwave has been discovered as an alternative way to solve this problem to save energy and time.

1.3 Objective

The objectives of this research is focus on the stability of crude oil emulsions and understand the mechanisms of the demulsification of crude oils using microwave heating technology.

1.4 Scope of Research

To accomplish the objective of this study, the scope of this research focuses on:

a) Characterization of emulsions in terms of chemical and physical properties such as shear stress, shear rate, viscosity, rotations per minute (rpm), temperature, surface tension and interfacial tension.
b) To examine the demulsification of water in crude oil emulsions by microwave heating using batch processes system.
c) To determine the temperature distributions at different locations (top, middle and bottom) for irradiated emulsions.
d) To study the effect of varying the microwave power generation at 720 and 540 watts.
e) Analyzing the overall potential of microwave demulsification as an alternative energy generation for water in crude oil emulsion demulsification.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

The formation of water-in-oil emulsions during production and transport of crude oils is a great problem challenging the petroleum industry. Tremendous research works are directed to understanding the mechanism of formation, stabilization, and controlling of oil field emulsions (Al-Sahhaf *et al.*, 2008). Microwave method used in demulsification process need to be done to remove water-in-crude oil emulsions, which cause corrosion in pipelines. There are many types of methods used such as heating (conventional method), usage of chemicals, membrane separation and microwave heating technology. Many parameters had been considered in the previous researches. This study enhances microwave heating technology by varying the power generation and usage of different emulsifier and demulsifiers.

2.2 Stability of Crude Oil

2.2.1 Mechanisms of Stabilization of Water-In-Crude Oil Emulsions

In this research, the mechanisms of stabilization of water-in-crude oil emulsions have been investigated by changing the solvent–solute interactions in crude oil. Diluting the original crude oil with varying amounts of heptane, which is a poor solvent for asphaltenes, changes the solvent–solute interactions, leading to flocculation of asphaltenes and thus changing the emulsion stability. The interactions between the water droplets in an emulsion system have been quantified by measuring the radial distribution function and thereby the pair potential using the digitized optical imaging technique. It has been observed that the force of interaction between water droplets is oscillatory. This shows that non-DLVO forces, such as attractive depletion and repulsive structural forces exist between the droplets. The interaction between the water droplets has been modeled by studying the properties of a thin liquid film sandwiched between the water droplets. Because of the film confinement effect, asphaltene–resin particles form a layered structure inside the thin liquid film. Also, the role of hydrodynamic interactions has been studied by using the film rheometer to measure the dynamic film tension and film elasticity. It has been found that, because of the adsorption of asphaltene at the film interfaces, the film elasticity plays a significant role in stabilizing these emulsions (Kumar *et al.*, 2001).

2.2.2 Water-In-Crude Oil Emulsions: Its Stabilization and Demulsification

Traditional ways of breaking emulsions using heat and chemicals are disadvantageous from both economic and environmental perspectives. In this research, the potential of microwave technology in demulsification of water-in-crude oil emulsions were investigated. The study produces some characterization studies to provide understandings of fundamental issues such as formulation, formation and breaking of emulsions by both chemical and microwave approaches. The goal of this research was to obtain optimized operating conditions as well as fundamental understanding of water-in-oil emulsion stability upon which further developments on demulsification processes could be developed. Experimental results found that microwave radiation method can enhance the demulsification of water-in-oil emulsions in a very short time compared to the conventional heating methods. The results obtained in this study have exposed that the capability of microwave technology in demulsification of water-in-oil emulsions (Abdurahman *et al.*, 2007).

In this research, it was found that emulsion stability was related to some parameters such as, the surfactant concentration, water content, temperature and agitation speed. Here, I will enhance this microwave heating technology by varying the power generation and usage of different emulsifier and demulsifiers.

Since water-in-crude oil emulsion creates many problem, especially foaming and corrosion in pipeline, many researches done to overcome this problem. From all the above researches, we can see that most of the researches were using complicated methods. Few researches used chemicals to demulsify water-in-crude oil emulsions, which may require additional cost and sometimes affect the chemical properties of the crude oil itself. So, to demulsify water-in-crude oil emulsions, it is required an easy, applicable, safe, cost effective method. So, I will be using microwave method in demulsification process to remove water-in-crude oil emulsions, which cause corrosion in pipelines.

2.2.3 Stability Investigation of Water-in-Crude Oil Emulsion

An experimental study was done by Abdurahman *et al.* (2006) to investigate the stability of water-in-crude oil emulsions in both creaming and coalescence states were measured as a function of sodium chloride concentration. The parameters measured in this research are salt concentration, mixing speed, water concentration and temperature.

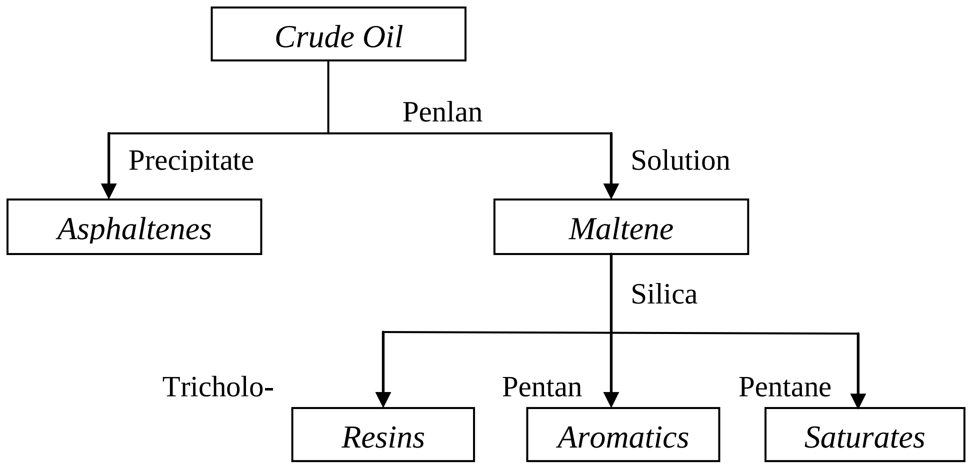

Fig 2.1 : Separation of crude oil fractions

Separation of water layer was used as a measure of physical instability for water-in-oil emulsions. Separated water was increased for emulsions having high salt concentrations. A long duration was necessary for separation of w/o emulsions with no heat and salt is remarkable for sedimentation experiments. However, an unstable emulsion could be eventually destroyed leading to complete separation of two phases.

From the interfacial tension measured in this research, it was discovered that the interfacial tension falls to low values at higher sodium chloride concentration. Other than that, density difference increases with salt concentration increase and consequently the interfacial tension decreases. Furthermore, with increasing of salinity of sodium chloride percentage, the chance for the molecules to collide with each other increases. It was discovered that as the volume fraction decreases, the separation time for water to separate from the emulsion decreased. Viscosity of the emulsion increases as surfactant concentration increases.

Viscosity of emulsion increases greatly as internal volume fraction increases, the result leads to emulsion stability. A surprising situation occurs where emulsion converted from w/o to o/w when the volume fraction reached certain level. In this study, when surface active agents added to the emulsions, the interfacially active agents were adsorbed or deposited at the interface of the o/w system. Other than that, in evaluation of temperature, emulsions were more stable when the temperature is near the point of minimum solubility of emulsifying agents. Emulsion stability decreases when temperature was increased.

In this stability investigation, the researchers focus on salt concentration, mixing speed, water concentration and temperature. In my research, I will be enhancing on more parameters but the similar parameter is the temperature and mixing speed (rpm).

2.3 Chemical Demulsification

2.3.1 Chemical Demulsification of Water-In-Crude Oil Emulsions

Chemical demulsification is the most widely applied method of treating water-in-crude oil emulsions and involves the use of chemical additives to accelerate the emulsion breaking process. The effect of chemical demulsification operations on the stability and properties of water-in-crude oil emulsions was assessed experimentally. Furthermore, influences of chemical demulsifiers on the destabilization of emulsions were studied in this research. Few chemicals such as Amine groups, Polyhydric Alcohol, Acid and Polymeric demulsifiers were used in this research as demulsifiers. Low sulfur Wax Residue (LWSR) and Triton X-100 were used to form emulsion in this study. These emulsifiers were not diluted before being used. Stability of the emulsions was determined at $30^{o}C$ as a function of time.

From this study, it was discovered that effect of amine group demulsifiers on crude oil emulsion stability (percentage water separation) increase with time. Decyl-amine has highest stability at the end of analysis and followed by Octyl-amine, Hexyl-amine, Pentyl-amine, Dioctyl-amine, Trioctyl-amine and Propyl-amine. Same data obtained for effect of amine group demulsifiers on crude oil emulsion stability (percentage oil separation). However, percentage oil separations for all amine group demulsifiers are higher compared to percentage of water separation. This was due to high molecular weight factor of amine which acts as flocculants in adsorption and interaction activities.

Data on the influence of polyhydric alcohols group on crude oil emulsion stability (percentage of water separation) shows that Polyethylene glycol (PEG) 1000 shows highest stability, whereas Ethylene glycol, PEG 600 and PEG shows stability in decreasing order. Emulsion stability of these alcohols on percentage of water separation is higher than percentage of water separation. This is because of low molecular weight alcohols are water soluble such as methanol and ethanol.

The researchers found out that influence of acid demulsifiers group on emulsion stability is higher for percentages of oil separation. In comparison, percentage of water separation in this category is lower for formic acid, butanoic acid and octanoic acid. Whereas, pentanoic acid, heptanoic acid and hexanoic acid shows very much lower than percentage of oil separation.

At the end of this research, the researchers discovered that all acid demulsifiers permit oil separation. Maximum percentage of separation occurs at 1340 mins compared to polyhydric demulsifiers group, acid demulsifiers were lower in both water and oil separations. It was also discovered that there is a strong correlation between good performance and the demulsifiers. Furthermore, the amine group demulsifiers promoted as the best coalescence of droplets at the end of the study. In contrast, polymeric demulsifiers group is the least in water separation (Abdurahman *et al.*, 2007).

This method takes very long time duration to complete demulsification of water in crude oil emulsions. So, I decided to choose faster and more effective method to separate water from crude oil emulsions, which is microwave heating technology.

2.3.2 Characterization and Demulsification of Water-in-Crude Oil Emulsions

The effect of chemical demulsifiers in demulsification of water-in-oil emulsions were assessed experimentally by Abdurahman *et al.* (2007). The relative rates of water separation were characterized via graduated beakers.